Reports

Estimate of the Contribution of Biologically Produced Dimethyl Sulfide to the Global Sulfur Cycle

Abstract. *Atmospheric dimethyl sulfide (DMS) measurements were made on the Atlantic Coast of the United States at Wallops Island and Cape Henry, Virginia, during June 1975. The very low concentrations, typically less than 30 parts per trillion observed at the Cape Henry site, were thought to result from the smog chemistry associated with the Norfolk metropolitan area. Atmospheric DMS concentrations at the Wallops Island site were much higher, having a geometric mean of 58 parts per trillion and a geometric standard deviation of 2.1. At this site the DMS source strength was estimated to be 6 milligrams of sulfur per square meter per year. Because of wind conditions during this experiment, the DMS source strength is thought to be representative of the DMS source strength of the ocean in the Wallops Island area and is much less than the 130 milligrams of sulfur per square meter per year needed to balance the ocean-atmosphere portion of the global sulfur budget.*

Biologically produced sulfur compounds are thought to account for one half of the total sulfur entering the atmosphere (*1, 2*). Despite the potentially great effect that these materials may exert on our climate and environment through their aerosol-forming properties (*3, 4*), our knowledge of these materials is very limited. Early investigators thought that H_2S was the primary sulfur carrier because this compound is produced in the decay processes of animal and plant tissue and by anaerobic microbial action in the sediments of lakes, marshes, and oceans. However, recent measurements of H_2S concentrations over land (*5*) indicated a background H_2S concentration of approximately 40 parts per trillion (ppt) by volume which, if we assume a mixing depth of 1 km and a residence time of 1 day (*4*), leads to an estimated source strength for land-based biologically produced H_2S of 2×10^{12} g year^{-1} or about 4 percent of the 58×10^{12} g of sulfur per year expected for land-based sources (*1*). Östlund and Alexander's studies (*6*) of the oxidation of H_2S in seawater indicated that, relative to its rate of diffusion from the sediments where it is thought to be generated, H_2S is quickly oxidized by the oxygenated surface layers of the ocean. This result implies that the biologically produced atmospheric H_2S arises only from land and shore areas and thus accounts for only 2×10^{12} g year^{-1} of the estimated 106×10^{12} g year^{-1} of the sulfur emitted into the atmosphere by biological sources (*1*).

The identity of the sulfur carriers thus remains to be determined. Lovelock *et al.* (*7*) have suggested that dimethyl sulfide (DMS) might be an important carrier since it is produced by some species of marine algae (*8*) and it has the required properties of volatility, insolubility in water, and stability toward oxidation by aqueous oxygen. They found that water in the North Atlantic is saturated with DMS and that some soils produce this compound. Their attempts to detect DMS in the atmosphere failed; however, they pointed out that oxidants trapped with DMS in their cryogenic trapping procedure could have destroyed the DMS before the analysis could be carried out.

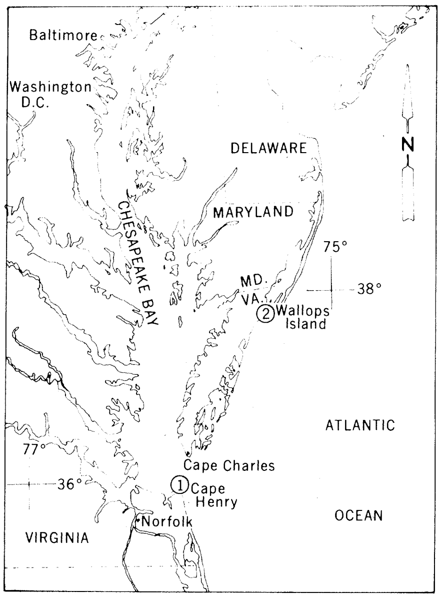

Fig. 1. Map showing the sites monitored in this study: site 1, Cape Henry; site 2, Wallops Island.

We have analyzed for DMS at two sites on the east coast of the United States (Fig. 1). Site 1 was located at Cape Henry, Virginia, near the mouth of Chesapeake Bay. Site 2 was located at the National Aeronautics and Space Administration launch facility at Wallops Island, Virginia. Wallops Island is a barrier island on the Virginia Eastern Shore near the Maryland border. Hourly measurements were made for 1 week at each site during June 1975. About 30 minutes was required to obtain each sample.

The DMS measurements were made with a gas chromatograph equipped with a flame photometric detector. The liquid phase in the column used to separate the sulfur compounds consisted of polyphenyl ether mixed with 0.1 percent H_3PO_4; Teflon beads (40/60-mesh) were used as support. We concentrated the sample by a factor of 330 before injecting it into the gas chromatograph by pulling about 1000 cm^3 of ambient air through a sample loop (3 cm^3) cooled to 87 K with liquid argon. The sample loop was a Teflon tube (1.8 m long, 0.20 cm in outside diameter) whose center portion was packed with 40/60-mesh glass beads. After a short cycle in which hot water was used to release the compounds from the glass beads, the carrier gas was diverted through the sample trap; in this way the sample was swept from the trap, through the column, and into the flame photometric detector. In calibrating the system, we used Teflon permeation tubes having known permeation rates. We carried out calibrations in the field environment by placing the permeation tubes directly in the sample manifold. The minimum concentration of DMS detectable by our method was approximately 10 ppt.

The concentrations of DMS at Cape Henry were typically less than 30 ppt. Many zero values were obtained, an indication that the instrument sensitivity was not great enough to characterize the distribution function for DMS at this site. However, measurable DMS concentrations were found most often when the wind was coming off the Chesapeake Bay. An unknown sulfur compound (compound U) having a retention time very close to that of CS_2 was observed concurrently with the DMS. A diurnal pattern was not observed for either DMS of compound U.

The concentrations of DMS were much higher at the Wallops Island site. The distribution of the DMS data for this site was clearly log-normal, and the measurements had a geometric mean of 58 ppt and a geometric standard deviation of 2.1. A few values exceeding 500 ppt were observed during early morning hours; these we attributed to the formation of strong low-level radiation inversions.

As expected, there was an approximately inverse relation between the DMS concentration at the Wallops Island site and the wind speed. A subgroup of DMS measurements made at wind speeds of less than 13 km hour^{-1} had a geometric mean of 70 ppt and a geometric standard deviation of 1.5; a similar grouping for wind speeds exceeding 20 km hour^{-1} had a geometric mean of 32 ppt and a geometric standard deviation of 1.7.

Although the nature of the sources expected to contribute to the DMS loading at the Wallops Island site had a high directional dependence, only a weak correlation between the DMS concentration and wind direction was observed. Table 1 summarizes the results of a statistical treatment of the DMS data subgrouped according to the wind direction at the time of measurement. Whereas open ocean should be the only important area source for subgroups with wind directions between 90° and 180° and between 180° and 220°, marshes, shallow bays, land, and open ocean can all be important area sources for the subgroup with wind direction between 0° and 90°. In view of the weak correlation between DMS concentration and wind direction, we conclude that for this site marshes, shallow bays, and land are not dramatically stronger sources of DMS than open ocean.

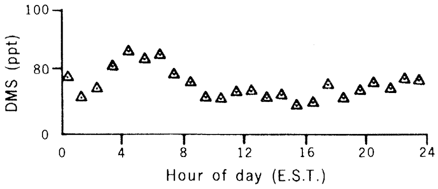

Fig. 2. Average diurnal variation in the DMS concentration at the Wallops Island site. Five data points were averaged to obtain each point shown on the graph.

The DMS data for Wallops Island clearly exhibited a diurnal pattern (Fig. 2). The DMS concentration increased from a minimum of 40 ppt near sundown to a maximum of 110 ppt near sunrise; after daybreak the DMS concentration decreased rapidly to about 40 ppt and then maintained this concentration for the remainder of the day. Lapse rates measured at 7 a.m. and 7 p.m. indicated that the diurnal pattern was determined primarily by low-level radiation inversions. Compound U was also observed at the Wallops Island site. It appeared concurrently with and at about the same concentration as the DMS.

The large differences in the DMS concentrations at the Cape Henry and Wallops Island sites are difficult to reconcile. Our Wallops Island data suggest that the ocean is an important source of DMS. The same ocean area that contributes to the DMS loading at the Wallops Island site with southwest winds can also contribute to the DMS loading at the Cape Henry site with northeast winds. The influence of the smog chemistry associated with the nearby Norfolk metropolitan area, however, might in part explain the low DMS concentrations found at Cape Henry. This thesis is supported by Cox and Sandalls's (*4*) observations that the DMS reactivity in smog systems is very great, being comparable to the reactivity of simple olefins such as propylene.

We have estimated the emission rate of DMS per unit area, using a method described by Shaffer (*9*) for determining the rate of emission of radon from soil. By analogy with Shaffer's treatment of the radon problem, we assumed that the DMS emission rate was constant over a wide area, that the DMS flux at 300 m during the nighttime was negligible, and that the DMS concentration at 300 m was constant at the daytime average DMS concentration. Under these conditions the DMS emission rate R is given by the expression (*9*):

$$R = -\frac{d}{dt}\int_0^{300} c\,dz \qquad (1)$$

where z is the vertical coordinate and c is the DMS concentration. By assuming that the DMS concentration decreased exponentially with height during the evening hours, we have evaluated the integral in Eq. 1 on an hourly basis between 6 p.m. and 6 a.m. A plot of the negative value of this integral as a function of time was a straight line whose slope yielded an emission rate for DMS of 6 mg of sulfur per square meter per year.

Table 1. Results of a statistical treatment of the DMS data for the Wallops Island site subgrouped according to wind direction.

Wind direction	Number of samples	Geometric mean concentration (ppt)	Geometric standard deviation	Area source description
0° to 90°	80	44	2.7	Marsh, shallow bays, land, ocean
90° to 180°	42	53	2.2	Open ocean
180° to 220°	47	62	1.7	Opean ocean
220° to 360°	0			Marshes, shallow bays, land

This emission rate for DMS is probably representative of the emission rate of this compound from the ocean near Wallops Island and is comparable to the 10 mg of sulfur per square meter per year obtained by Liss and Slater (*10*), using the DMS data of Lovelock *et al*. (*7*) and a two-layer model for gaseous transport across the air-sea interface. Both of these estimates are much smaller than the average emission rate for biological sources of 130 mg of sulfur per square meter per year (*1*) required to balance the ocean-atmosphere portion of the global sulfur cycle. Therefore, unless the emission rate of DMS is much larger for other areas of the ocean, it would appear that DMS from ocean sources makes a very small fractional contribution to the global sulfur cycle.

PETER J. MAROULIS
ALAN R. BANDY
Department of Chemistry,
Drexel University,
Philadelphia, Pennsylvania 19104

References

1. J. P. Friend, in *Chemistry of the Lower Atmosphere*, S. I. Rasool, Ed. (Plenum, New York, 1973), chap. 4.
2. C. E. Junge, *Air Chemistry and Radioactivity* (Academic Press, New York, 1963); E. Robinson and R. C. Robbins, "Sources, abundances and fate of gaseous atmospheric pollutants" (Project Report PR-6755, Stanford Research Institute, Menlo Park, Calif., 1968); W. W. Kellogg, R. D. Cadle, E. R. Allen, A. L. Lazrus, E. A. Martell, *Science* **175**, 587 (1972).
3. R. D. Cadle, in *Chemistry of the Lower Atmosphere*, S. I. Rasool, Ed. (Plenum, New York, 1973), chap. 2.
4. R. A. Cox and F. J. Sandalls, *Atmos. Environ.* **8**, 1269 (1974).
5. D. F. S. Natusch, H. B. Klonis, H. D. Axelrod, R. J. Teck, J. P. Lodge, Jr., *Anal. Chem.* **44**, 2067 (1972).
6. H. G. Östlund and J. Alexander, *J. Geophys. Res.* **68**, 3995 (1963).

J. E. Lovelock, R. J. Maggs, R. A. Rasmussen, *Nature (London)* **237**, 452 (1972).

8. F. Challenger, *Adv. Enzymol.* **12**, 429 (1951).
9. W. A. Shaffer, thesis, Drexel University (1973).

P. S. Liss and P. G. Slater, *Nature (London)* **247**, 181 (1974).

23 March 1976; revised 15 November 1976